



Activation or passivation: Influence of halogen dopant (F, Cl, Br) on photothermal activity of Mn_2O_3 in degrading toluene

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ABSTRACT

Mn_2O_3 is an exceptional earth-abundant mineral that has been extensively applied in catalytic oxidation because of the strong redox couples like $\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{Mn}^{4+}/\text{Mn}^{3+}$ exposed on Mn_2O_3 surface. Herein, the catalytic activity of Mn_2O_3 in photothermal degradation of toluene was regulated by halogens including F⁻, Cl⁻ and Br⁻. As the electronegativity ordered in F (3.98) > O (3.44) > Cl (3.16) > Br (2.96), F⁻ doped Mn_2O_3 overperforms Cl⁻ doped and Br⁻ doped Mn_2O_3 in decomposing toluene. DFT theoretical calculation illustrates that F⁻ attracts the shared electrons from Mn to itself, the deviated charge center stretches the adjacent Mn-O bonds and boosts the generation of abundant oxygen vacancies, helping to strengthen the catalytic activity of Mn_2O_3 . Conversely, Mn-O bonds are shortened by Cl⁻ and Br⁻ that have lower electronegativity than O. The multiple electrons circling Cl⁻ and Br⁻ push Mn towards O and squeeze Mn-O bonds, resulting in the formation of passivated Mn_2O_3 . In conjunction with Mn redox couples and oxygen vacancies, 99% of 400 ppm toluene can be eliminated by F⁻ doped Mn_2O_3 , corresponding mineralization rate is high up to 95.8%.

1. Introduction

Volatile organic compounds (VOCs), are mainly human-made chemicals that have a high vapor pressure and low water solubility. The origin of VOCs contains indoor sources and outdoor sources. For instance, building materials (paint, adhesives, pressed wood products), home and personal care products (pesticides, fuel oil, gasoline), as well as activities like smoking, wood burning in stoves, dry-cleaned clothing contribute to indoor air pollution. Industrial emissions, diesel emissions, and oil and gas extraction and processing account for outdoor air pollution. Breathing VOCs probably present a health risk, especially those long-term exposures to benzene, toluene, and formaldehyde that give rise to cancer [1,2]. Toluene, one of the representative aromatic hydrocarbons, has numerous commercial and industrial applications: it is a common solvent in paints, lacquers, thinners, glues, correction fluid, and nail polish remover, as well as in printing and leather tanning procedures [3]. Its wide variety of purposes makes it ubiquitous in atmospheric circumstances. However, inhaling, direct contact, and ingestion bring harmful influences for human beings. Thereby, scientists have placed a premium on cleaning toluene from the air by exploring various techniques that can be classified into two categories: physical

methods and chemical methods. Adsorption with active carbon [4], and membrane separation [5] are included in a physical group, for they only transfer toluene from one place to another without changing their molecular structures. Thermal catalysis [6,7], plasmonic catalysis [8,9], photocatalysis [10,11], photo-thermal catalysis [12,13], and biodegradation technologies [14,15] that can render decomposition of toluene are defined as chemical techniques. Among them, photo-thermal catalysis is an emerging technology using sunlight as an energy source to increase catalyst temperature and trigger chemical reactions, which realizes energy-saving and high efficiency through merging the advances of photocatalysis and thermal catalysis. During photothermal catalysis, upon harvesting solar lights, semiconductor catalysts are capable of converting light energy into heat by demonstrating a broad absorption of the solar spectrum. Simultaneously, they are excited to generate excitons that will be responsible for photocatalysis. As a consequence of conjugating countless active and heated sites, converting toluene is speeded up and toluene molecules can be turned in non-toxic CO_2 and H_2O under mild conditions [16].

Plasmonic catalysts like noble metal nanoparticles engineered semiconductors generally deliver attractive photothermal catalytic activity because of the localized surface plasmon resonance (LSPR) effect

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[17]. Compared with plasmonic noble metal NPs mediated catalysts, activated carbon (AC)/graphitic carbon nitride (CN) composites [18], $\text{CeMn}_x\text{O}_y/\text{TiO}_2$ [19], $\text{Co}_3\text{O}_4/\text{TiO}_2$ [20], $\text{CeO}_2/\text{LaMnO}_3$ [21] composites are also able to transfer photos into heat by demonstrating an outstanding photo-thermal catalytic performance, which can compete with plasmonic catalysts.

Manganese oxide (MnO_x) is another promising candidate for photo-thermal catalytic degradation of VOCs due to its excellent activity, good stability, and low cost [22]. The electrons transfer between Mn^{2+} , Mn^{3+} , and Mn^{4+} greatly contributes to the superior catalytic performance of MnO_x during thermal catalysis [23]. For instance, manganese oxide octahedral molecular sieves (OMS-2) exhibited excellent catalytic performance for benzene oxidation by a great deal of oxygen vacancy and its ability in converting solar energy to thermal energy [24]. Mn_2O_3 composites including LaMnO_3 [21], $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ [25], FeMnO_3 [26], NiMnO_3 [27] and $\text{SmMnO}_3/\text{CuMnO}_x$ [28] demonstrate remarkable photothermal efficacy in removing organic chemicals. Besides the redox couples of Mn, it is found that oxygen vacancy (Ov) in MnO_x accounts for the final degradation efficiency [29,30]. OV is the most active sites in photocatalysis, which boosts the generation of superoxide radical ($\bullet\text{O}_2^-$) that account for the strengthened adsorption and degradation of target pollutants. Generally, OV is created by replacing lattice oxygen with foreign species such as doping or constructing heterojunctions [31]. In Yang's work [32], they controlled the mole ratio of O to Cl through tuning the glucose amount, generating $\text{Cu}_2\text{O}-\text{CuCl}$ composites with plentiful OV. BiOX (where $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) are regulated with abundant oxygen vacancy defects owing to X dopant, having superior capacity in adsorbing and activating CO_2 molecules [33]. Fluorine was first used to improve the activity of TiO_2 by adding a small amount of trifluoroacetic acid (TFA) into the sol-gel (SG) starting solution [34]. It was found that fluorine would influence the photocatalytic reactions by changing the interfacial e^-/h^+ transfer, surface charge distribution, and substrate-surface interaction, which were attributed to the enhancement of surface acidity, formation of surface hydroxyl radicals, and creation of oxygen vacancies [35]. The F atom tends to substitute lattice O atom in metal oxide because of the similar size compatibility [36]. The aforementioned studies suggest that doping halogens in photocatalysts are efficient and feasible in creating OV.

Though halogens are common in many precursors for synthesizing MnO_x catalysts and are probably residual in MnO_x , there is no related work about elucidating the influence of fluorine, chlorine, bromine ions on MnO_x 's activity and the involved mechanism from the perspective of halogen's electronegativity. Inspired by that, F^- , Cl^- , and Br^- were doped in Mn_2O_3 and corresponding performance was assessed by applying halogen- Mn_2O_3 in toluene degradation under simulated full-spectrum solar lights. It's found that many more oxygen vacancies are created as Mn_2O_3 is doped with F^- on the strength of the marvelous property of attracting shared electrons, which helps to boost the removal efficiency of toluene. As for Cl^- and Br^- , the opposite impact is observable. For the sake of large size and lowered electronegativity compared with O, their doping causes shortened and reinforced Mn-O bonds, which passivates Mn_2O_3 and blocks the active sites, resulting in declined degradation efficacy. This study highlights the influence of fluorine, chlorine, bromine ions upon the photothermal activity of Mn_2O_3 catalysts, figuring out the root cause for the variability using different manganese salts with halogen ions contained.

2. Experimental

2.1. Chemicals

Manganese fluoride (MnF_2) was purchased from Shanghai Yuanye Bio-Technology Co., Ltd. Manganese chloride hexahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 99.99%), Manganous acetate tetrahydrate ($\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$), and ethanedioic acid dihydrate ($\text{C}_2\text{H}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Manganese

bromide tetrahydrate ($\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$, 99.99%) was purchased from Aladdin Reagents (Shanghai) Co., Ltd. All these chemicals were of analytical grade and used without further purification.

2.2. Synthesis of catalysts

Mn_2O_3 and Mn_2O_3 doped with fluorine, chlorine, bromine was synthesized by the co-precipitation method. 50 mmol $\text{C}_4\text{H}_6\text{MnO}_4$ was dissolved in a beaker with 100 mL of deionized water and the solution was kept stirring for 15 min; 60 mmol $\text{C}_2\text{H}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ that was ensured Mn^{2+} was completely precipitated was dissolved in 100 mL of deionized water. The prepared $\text{C}_2\text{H}_2\text{O}_4$ solution was dropped wisely added to the $\text{C}_4\text{H}_6\text{MnO}_4$ solution, which was then stirred for 30 min to form a milky MnC_2O_4 suspension. The as-prepared MnC_2O_4 was dried at 60°C for 8 h and then calcined at 500°C in static air for 2 h (heating rate $5^\circ\text{C}/\text{min}$) to obtain Mn_2O_3 (denoted as Mn_2O_3).

$\text{Mn}_2\text{O}_3\text{-F}$ (0.1 mol), $\text{Mn}_2\text{O}_3\text{-Cl}$ (0.1 mol), and $\text{Mn}_2\text{O}_3\text{-Br}$ (0.1 mol) were synthesized in the same way as above with changing partial manganese precursor as MnF_2 , $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$. Taking F^- doped Mn_2O_3 as an example kept the total molar amount of Mn (50 mmol) unchanged and regulated the molar ratio of MnF_2 to $\text{C}_4\text{H}_6\text{MnO}_4$ as 6:4, 4:6, 3:7, 2:8, respectively. The corresponding engineered Mn_2O_3 with different fluorine content was labeled as $\text{Mn}_2\text{O}_3\text{-F}$ (0.06 mol), $\text{Mn}_2\text{O}_3\text{-F}$ (0.04 mol), $\text{Mn}_2\text{O}_3\text{-F}$ (0.03 mol), and $\text{Mn}_2\text{O}_3\text{-F}$ (0.02 mol).

2.3. Characterization

XRD patterns of Mn_2O_3 and halogen doped Mn_2O_3 were obtained with a Bruker D8 Advance X-ray diffractometer (Bruker, Germany) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$). Atomic ratios of elements in Mn_2O_3 catalysts were analyzed by an energy-dispersive portable X-ray Fluorescence Spectrometer (XRF) using a PANalytical Axios configured in a laboratory accessory stand. X-ray photoelectron spectroscopy (XPS) analyses were carried out in an ultrahigh vacuum chamber with a pressure of 2×10^{-9} bar at room temperature (Thermo Fisher Scientific, ESCALAB 250). The morphology and microstructures of catalyst were observed with the transmission electron microscope (TEM) (FEI Talos F200X) and scanning electron microscopy (SEM) (Hitachi, model SU1510). UV-Vis-IR spectrophotometer (UV-3600 plus) was employed to record the full-spectrum light absorption on Mn_2O_3 catalysts. EPR and ESR spectra were obtained through an electron paramagnetic resonance spectrometer (Bruker A300). Laser Raman spectrum was measured with Ar ion laser as the excitation source, and the test range was about $50\text{--}800 \text{ cm}^{-1}$ frequency band (HORIBA Jobin Yvon S. A. S.). H_2 temperature-programmed reduction ($\text{H}_2\text{-TPR}$) and O_2 temperature-programmed desorption ($\text{O}_2\text{-TPD}$) were carried out on the AutoChem1 II 2920 chemical adsorption analyzer. The temperature images were measured using a FLIR infrared thermometer. The relative humidity was measured using a humidity/temperature transmitter (HMT130). The BET adsorption and desorption isotherms were performed on a Belsorp-Mini II analyzer (Japan), which relative uncertainty is $\pm 7\%$. A thermocatalytic reaction was carried out in a thermostatic heating jacket (ZNCL-T). Gas chromatography (GC, Agilent Technologies 7890A) was used to detect the concentration of toluene and CO_2 in the catalytic process, and gas chromatography-mass spectrometry (GC-MS, Agilent Technologies 7890A-5975C) was used to identify the specific components in the reactor during the catalytic process.

2.4. Photothermal degradation of toluene with Mn_2O_3 and halogen- Mn_2O_3

The solar light-driven thermocatalytic oxidation of toluene was performed in a closed cylindrical stainless steel gas-phase reactor (450 mL) equipped with a quartz window (110 mm in diameter). In the reactor, the air was regulated according to the components in actual air. The content of N_2 is 78%, that of O_2 is 21%, and the relative humidity

ranges from 5% to 100%. The reactor was connected to a GC-MS gas chromatograph (GC) equipped with a flame ionization detector (FID) for in-situ monitoring intermediates generated during toluene degradation. 0.1000 g catalyst was uniformly coated on a glass fiber filter membrane (50 mm in diameter and 0.1 μm aperture), which was subsequently placed on the reactor bottom. A 300 W Xe lamp (Perfect Light, PLS-SXE300) was placed above the quartz window to provide UV-Vis-NIR lights (Light intensity: 398 mW/cm^2). The temperature change during the reaction was determined by a FLIR infrared thermometer.

CO_2 increasement was taken as an indicator to evaluate the mineralization degree of toluene. As there are CO_2 molecules in the air and the catalysts can adsorb CO_2 , the reactor needed to be irradiated for 15 min to reach a steady CO_2 baseline for the subsequent determination of CO_2 increment, and then turned off the light. Soon after that, 0.86 μL of liquid toluene was injected into the reactor through an inlet embedded in the hermetic seal. The calculated initial toluene concentration is about 400 ppm. 5 min later, after all the toluene molecules evaporated, turned on the lamp, and started the degradation. CO_2 increment was recorded by subtracting the initial CO_2 content (before catalysis) in the reactor, and the corresponding removal percentage of toluene was calculated. Repeated runs were conducted under the same conditions after renewing the reactor with fresh air.

2.5. DFT theoretical calculation

We employed a Vienna Ab Initio Package (VASP) [37,38] to perform all the density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the PBE formulation [39]. The projected augmented wave (PAW) [40,41] potentials were employed to describe the ionic cores and take valence electrons into account using a plane-wave basis set with a kinetic energy cutoff of 450 eV. Partial occupancies of the Kohn-Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was lower than 10^{-4} eV. Geometry optimization was considered convergent when the force change was less than 0.05 eV/Å. Grimme's DFT-D3 methodology was used to describe the dispersion interactions [42]. The equilibrium lattice constants of the Mn_2O_3 unit cell were optimized when using a $5 \times 5 \times 5$ Monkhorst-Pack k-point grid for Brillouin zone sampling. The vacuum spacing perpendicular to the plane of the structure was 20 Å. The Brillouin zone integral uses the surfaces structures of $3 \times 3 \times 1$ monkhorst pack K point sampling for surfaces. The formation energies of O was calculated as follow:

$$E_f = E_{\text{total}} - \frac{1}{2}E_{\text{O}_2} + xE_B$$

where the E_{total} is Mn_2O_3 with M (F, Cl, Br) doping energy with O defect and E_B is the structure energy, E_{O_2} is the O_2 energies. The adsorption energies (E_{ads}) were calculated as:

$$E_{\text{ads}} = E_{\text{ad/sub}} - E_{\text{ad}} - E_{\text{sub}}$$

where $E_{\text{ad/sub}}$, E_{ad} , and E_{sub} are related to the optimized adsorbate/substrate system, the adsorbate on the catalyst surface, and the clean substrate, respectively.

3. Results and discussion

3.1. Morphological and structural characterization of Mn_2O_3 and Mn_2O_3 -halogen

XRD patterns (Fig. 1) show that Mn_2O_3 catalysts doped with F[−], Cl[−], Br[−] display almost the same diffraction peaks as those of pristine Mn_2O_3 . The specific peaks located at 66.2°, 55.3°, 49.5°, 45.5°, 38.8°, 33.1°, and 23.3° correspond to the crystal planes of (622), (440), (431), (332), (400), (222), and (211), respectively, which are indexed to cubic bixbyite Mn_2O_3 [43]. Nevertheless, compared with pristine Mn_2O_3 , the enlarged diffraction peaks at 33.1° exhibit that the (222) plane of Mn_2O_3 -F positively shifts, indicating a shrank lattice spacing. As for Mn_2O_3 -Cl and Mn_2O_3 -Br catalysts, slightly negative shifts are observable, suggesting the lattice spacings along (222) planes are widened.

Based on the XRD data in Fig. 1, the lattice constant values (a) of pristine and halogen-doped Mn_2O_3 were calculated using the following equation [44]:

$$d^2 = \frac{a^2}{h^2 + l^2 + k^2}$$

Where d is the interplanar distance, a is the lattice parameter, and h, k, l are the miller indices of the crystal plane. Since α - Mn_2O_3 is a cubic phase, the lengths a, b, and c of the three cell edges are equal. As shown in Table S1, the edge length of Mn_2O_3 unit cell is decreased from 9.4091 Å to 9.3955 Å in Mn_2O_3 -F while those in Mn_2O_3 -Cl and Mn_2O_3 -Br are prolonged to 9.4222 Å and 9.4227 Å, respectively. Fig. 1 and Table S1 verify the lattice contraction aroused by F[−] and lattice expansion triggered by Cl[−] and Br[−].

The effect of increased calcination temperatures was studied. As Fig. S1 depicted, a higher temperature treatment enables a higher crystallinity of Mn_2O_3 with strong Mn-O covalent bonds, which will

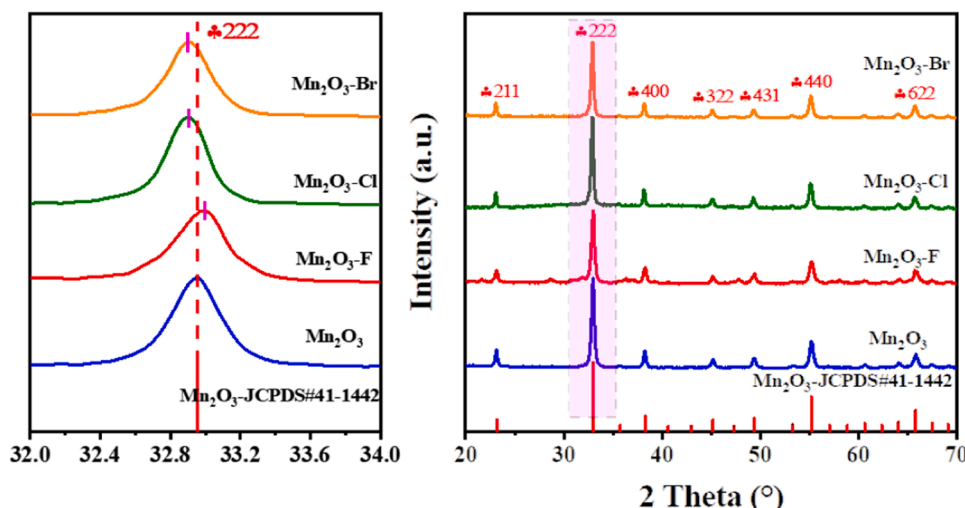


Fig. 1. XRD patterns of pristine Mn_2O_3 and Mn_2O_3 doped with F[−], Cl[−], Br[−].

make it difficult for halogens to bond with Mn. Our investigation validates that 500 °C is the optimal calcination temperature for synthesizing pure Mn_2O_3 with suitable crystallinity. Depicted as Fig. S1a, the products are predominantly Mn_3O_4 when the MnC_2O_4 (0.1 mol F) precursor was subjected to calcination at 400 °C. As the temperature increased to 600 °C, the crystallinity of Mn_2O_3 is notably enhanced. Consequently, the content of OV in Mn_2O_3 is less than that sintered at 500 °C (Fig. S1b). Moreover, the bond predominates in the halogen- Mn_2O_3 compound is still a covalent bond, for the Mn-Cl bonds are in small quantities.

Although SEM images of Mn_2O_3 and halogen- Mn_2O_3 (Fig. 2) exhibit that the as-prepared are big blocks covered with cracks, the nitrogen adsorption-desorption isotherms (Fig. S2) of the different Mn_2O_3 catalysts show type-IV curves with H3 hysteresis loop at relatively high pressure ($0.6 \leq P/P_0 \leq 1.0$), demonstrating the mesoporous features [21]. Listed as Table S1, the Brunauer-Emmett-Teller (BET) surface area of Mn_2O_3 is 16.9 m^2/g , doping F^- (0.03 mmol in precursor) in Mn_2O_3 improves BET to 32.4 m^2/g . The total pore volume is increased from 0.18 to 0.27 cm^3/g , and the average pore diameter is shrunk from 41.5 to 33.5 nm. However, doping Cl^- and Br^- in Mn_2O_3 brings a negative impact on Mn_2O_3 construction. The specific surface area of $\text{Mn}_2\text{O}_3\text{-Cl}$ and $\text{Mn}_2\text{O}_3\text{-Br}$ are less than 10 m^2/g . As Cl^- and Br^- have larger ion radii than F^- , their doping contents in Mn_2O_3 are minor than that of F^- in Mn_2O_3 . Except those implanted in Mn_2O_3 , some residual Cl^- and Br^- are adsorbed on the Mn_2O_3 surface, covering the active centers [45]. Moreover, during the synthesis process of $\text{Mn}_2\text{O}_3\text{-Cl}$ and $\text{Mn}_2\text{O}_3\text{-Br}$, the dispersed Cl^- and Br^- also suppress the cleavage of crystals and the generation of small particles during calcination [46], leading to the decline in specific surface areas.

TEM images in Fig. 2 present the details of structural varies caused by

halogen doping. As shown, all the Mn_2O_3 catalysts are in nanoparticle form, which tends to aggregate to form a mesoporous interface. Although the nanoparticles are in irregular shapes, their diameters are less than 10 nm. Comparing the high-resolution TEM images, the lattice spacing indexed to (222) planes in $\text{Mn}_2\text{O}_3\text{-F}$ is 0.263 nm, less than the 0.272 nm in pristine Mn_2O_3 , while those among $\text{Mn}_2\text{O}_3\text{-Cl}$, $\text{Mn}_2\text{O}_3\text{-Br}$ lattice fringes are 0.274, 0.276 nm, respectively, increased by 0.002 and 0.004 nm as compared with the standard 0.272 nm.

The variation in Mn_2O_3 structure posed by F^- doping is more significant than Cl^- and Br^- doping, and the changing trends in lattice spacing are in accordance with the XRD analysis. Moreover, as the elemental mapping pictures (Fig. 2) of F^- , Cl^- , and Br^- show, the loading content of F^- in Mn_2O_3 is much higher than those of Cl^- and Br^- . That's because F^- is the smallest, its diameter is 0.133 nm, almost as same as that of O^{2-} (0.14 nm), which enables F^- to enter Mn_2O_3 lattice and replace O more easily. It was also reported that the heteroatom tends to substitute an atom with the same approximate valence state and size compatibility [47]. Concerning Cl^- (0.181 nm) and Br^- (0.196 nm), their large sizes hinder the insertion in Mn_2O_3 , leading to low doping contents. Since XRF is a rigorous method for ascertaining the contents of elements in the matrix, it was employed to determine the atomic ratio of F, Cl, and Br in Mn_2O_3 catalysts. As shown in Table S2, the atomic ratios of F, Cl, Br in $\text{Mn}_2\text{O}_3\text{-F}$, $\text{Mn}_2\text{O}_3\text{-Cl}$, $\text{Mn}_2\text{O}_3\text{-Br}$ determined by XRF are 6.42%, 4.28%, and 1.98% accordingly, minimized with the increased ionic radius of F, Cl, and Br. XPS and TEM analysis on element contents were conducted as well. Relating results in Table S2 show that although the specific values from different strategies are variable, they demonstrate the same tendency, which confirms that F^- can be implanted in Mn_2O_3 with higher contents due to its smallest size.

Nevertheless, depicted in Fig. S3, overloading of F^- in Mn_2O_3 causes

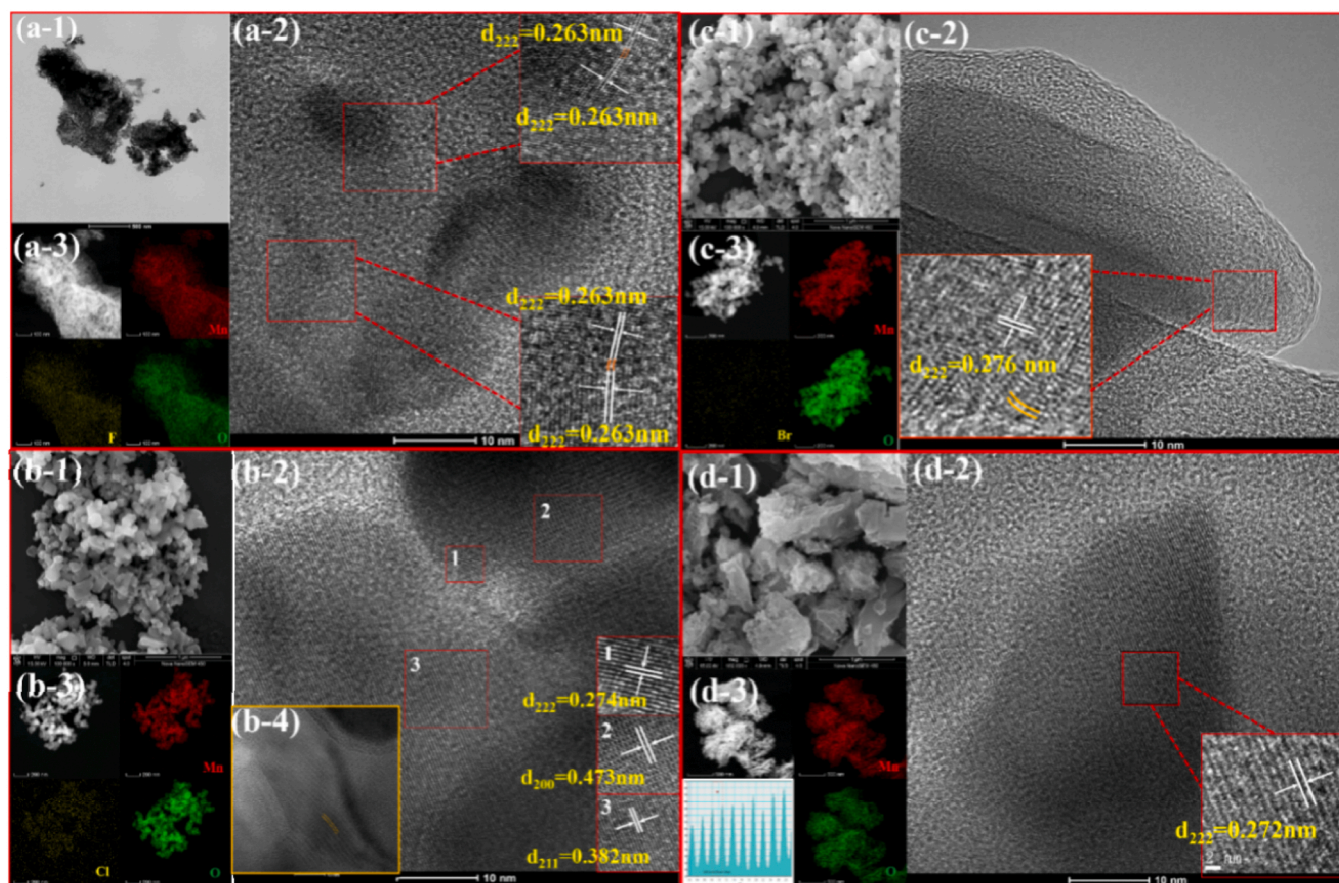


Fig. 2. SEM, HRTEM, and EDS phase mapping of the Mn (red), halogen (yellow), and O (green) distributions images of the (a) $\text{Mn}_2\text{O}_3\text{-F}$, (b) $\text{Mn}_2\text{O}_3\text{-Cl}$, (c) $\text{Mn}_2\text{O}_3\text{-Br}$, and (d) Mn_2O_3 catalysts.

declined crystallinity along (222) planes. Increasing Cl⁻ and Br⁻ dopant pose the same results as that of F⁻.

3.2. Textural property of as-prepared Mn₂O₃ and halogen-Mn₂O₃

XPS spectra of Mn 2p in Fig. 3a show characteristic peaks centered at 641.79 eV and 653.51 eV, which are assigned to Mn 2p 3/2 and Mn 2p 1/2, respectively. Each peak can be deconvoluted into three peaks according to the binding energies of Mn species, Mn²⁺, Mn³⁺, and Mn⁴⁺ [48]. Compared with pristine Mn₂O₃, the binding energies of Mn 2p in Mn₂O₃-F positively shift by 0.89 eV, for the sake of decreased electron density around Mn. The root cause behind this is the high electronegativity of F. It's known that electronegativity, symbolized as X, is the tendency for an atom to attract shared electrons (or electron density) when forming a chemical bond. The electronegativity of F is the strongest among all the elements. X(F) is 3.98, higher than X(O) 3.44. When O²⁻ in Mn₂O₃ is replaced by F⁻, the electrons circling Mn are attracted by F⁻ and incline to F⁻, leading to the increased binding energy of valence electrons in Mn 2p orbits. The opposites occur in presence of Cl⁻ and Br⁻ doping because X(Cl) is 3.16, X(Br) is 2.96, both less than X(O).

Furthermore, the redox couples, Mn²⁺/Mn³⁺ and Mn³⁺/Mn⁴⁺, in Mn₂O₃ help to transfer photogenerated electrons among Mn²⁺-Mn³⁺-Mn⁴⁺ circle for benefiting the photocatalysis [49]. The proportions of Mn^{x+} (x = 2, 3, 4) on the MnO_x surface determine the surface oxygen species [50]. In general, numbers of surface adsorbed oxygen species like O²⁻ or O⁻ rely on Mn⁴⁺ content. And Mn²⁺ accounts for the production of oxygen vacancy. Therefore, high contents of Mn⁴⁺ and Mn²⁺ will strengthen the oxidizing capacity of MnO_x. According to the Mn 2p XPS spectra (Fig. 3a), the proportions of Mn²⁺, Mn³⁺, Mn⁴⁺ were calculated through quantitative analysis, corresponding data are listed in Table S3. Among all the halogen-doped Mn₂O₃ catalysts, F⁻ dopant boosts the most notable enhancement in the contents of Mn²⁺ and Mn⁴⁺, accompanied by the lowest Mn³⁺ contents. The proportions of Mn²⁺, Mn³⁺, Mn⁴⁺ in the pristine Mn₂O₃ are 2.44%, 54.72%, and 42.83% in sequence, which vary as 5.21%, 43.25%, and 51.64% in Mn₂O₃-F, verifying the active role of F⁻ dopant.

Fig. 3b shows the UV-Vis-NIR absorption spectra of different Mn₂O₃ catalysts which are all sensitive to full-spectrum light. The strong absorption bands in wavelength ranges of 250–300, 650–750, 1350–1450, and 2100–2400 nm are observable, and Mn₂O₃-F demonstrates the optimal capacity of light harvest. Temperature images are captured using a FLIR infrared thermometer. As the inset in Fig. 3b displays, under irradiation, the temperatures of Mn₂O₃, Mn₂O₃-F, Mn₂O₃-Cl, and Mn₂O₃-Br reach 198 °C, 213 °C, 196 °C, and 199 °C, respectively. Although the four catalysts display similar absorption peaks within the full-spectrum light region, only F⁻ doping realizes the enhancement in photothermal conversion, which can be ascribed to the increasing structural defects and the increased Brunauer-Emmett-Teller (BET) surface areas of Mn₂O₃ [51,52].

H₂ temperature-programmed reduction (H₂-TPR) profiles depicted in Fig. 3c exhibit two reduction peaks, the one located at 332 °C is from Mn⁴⁺ being reduced to Mn³⁺, the other at 441 °C stands for the conversion of Mn³⁺ to Mn²⁺, which illustrates the stepwise reduction of Mn₂O₃ to Mn₃O₄, and ultimately to MnO [43]. Usually, the temperature for Mn₂O₃ transforming in Mn₃O₄ is used to evaluate the reduction capacity of Mn₂O₃. Compared to the pristine Mn₂O₃, doping F⁻ Mn₂O₃ can enable Mn ions reduced at lower temperatures, implying that Mn₂O₃-F can accept electrons more easily than Mn₂O₃. On the contrary, the elevated temperatures presented by Mn₂O₃-Cl and Mn₂O₃-Br suggest that Mn₂O₃ is passivated by Cl⁻ and Br⁻. And concerning the effect of doping amount of F⁻ amount, the most significant decrease of temperature is achieved on Mn₂O₃-F (0.03 mol). O₂ temperature-programmed desorption (O₂-TPD) analysis was performed to identify the types of oxygen species in Mn₂O₃ for exploring the potential factors affecting the reduction properties [48]. Generally, the oxygen species (peroxide species, O₂⁻) can be classified as the surface oxygen species (<350 °C),

active lattice oxygen species (monatomic species, O⁻) near the surface (350–550 °C), and lattice oxygen species (also known as O²⁻ species, >550 °C) [43]. Much attention has focused on the first two because lattice oxygen species (O²⁻ species, >550 °C) often become inert during toluene oxidation at low temperatures [53]. Profiled as Fig. 3d, all Mn₂O₃-F candidates display intense signals (active lattice oxygen species) sited at 526 °C, which manifests the exceptional oxidizing capacity of Mn₂O₃-F. As for Mn₂O₃-Cl and Mn₂O₃-Br, they exhibit declined performance than the pristine Mn₂O₃.

A theoretical model was established with density functional theory (DFT) to further illuminate the influence mechanism of halogen doping. In the light of Fig. 3e, the calculated band energy of Mn-O in original Mn₂O₃ is 206.63 kJ/mol, which goes down to 172.96 kJ/mol in Mn₂O₃-F along with the Mn-O bond length extends from 2.37 Å to 2.44 Å. The various evidence that F⁻ weakens the adjacent Mn-O bonds by stretching them, signifying Mn₂O₃ is activated. However, because of the lower electronegativity compared with O (3.44) and the big ion radius, doping Mn₂O₃ with Cl (3.16) and Br (2.96) renders shortened Mn-O bands in Mn₂O₃-Cl and Mn₂O₃-Br: 2.24 Å for Mn₂O₃-Cl, 2.21 Å for Mn₂O₃-Br, presented as increased bond energies: 219.24 kJ/mol and 232.14 kJ/mol, respectively. The reinforced Mn-O bonds will be hard to be broken and difficult to supply active lattice oxygen.

3.3. Catalytic performance in the degradation of toluene under different conditions

To address the synergetic catalytic performance, photocatalytic, thermal catalytic, and full-spectrum-light driven photothermal degradation of toluene was carried out to evaluate the impact of F⁻, Cl⁻, and Br⁻ on the catalytic activity of Mn₂O₃, with results shown in Fig. 4a and b. It is found that photocatalysis and thermal catalysis are not as effective as photothermal catalysis. The photothermal removal percentage of toluene on variable Mn₂O₃ catalysts is ordered as Mn₂O₃-F (0.1 mol) (99%) > Mn₂O₃ (85%) > Mn₂O₃-Cl (0.1 mol) (55%) > Mn₂O₃-Br (0.1 mol) (52%). Of note, mineralization endowed by Mn₂O₃-F is high up to 89%, much superior to Mn₂O₃ (72%), Mn₂O₃-Cl (26%), and Mn₂O₃-Br (24%). F⁻ doping remarkably improves the final catalytic efficiency in detoxifying toluene by converting it to CO₂ and H₂O, while Cl⁻ and Br⁻ bring negative influence. Combining the results in Fig. 3, we conclude that the activated Mn-O bonds in Mn₂O₃-F play a pivotal role in accelerating the decomposition of toluene.

Fig. 4c and d exhibit that the removal percentage of toluene is improved as the F⁻ content in Mn₂O₃ increased, after reaching the vertex in presence of Mn₂O₃-F prepared with 0.03 mol of F⁻ in precursor, it declines in that over-doping F⁻ in Mn₂O₃ could cover and block the active sites implanted in Mn₂O₃ [54]. With the best Mn₂O₃-F (0.03 mol in precursor), the toluene degradation efficiency is 99%, and the mineralization degree is high up to 95.8%. In the following section, all the Mn₂O₃-F mentioned is the optimal one.

We tested the catalytic activity of the Mn₂O₃-F in degrading toluene under irradiation of ultraviolet-visible-infrared, visible-infrared and infrared lights by using different cutoff filters, with results in Fig. 5a and b. The difference in the degradation percentage of toluene under different lights is not notable, but the variability regarding mineralization degree is significant. Driven by UV-Vis-NIR lights, the CO₂ yield is 131.78 mg m⁻³ min⁻¹, and that under visible lights (wavelength > 420 nm) is 117.95 mg m⁻³ min⁻¹. When only NIR lights above 780 nm are applied, the CO₂ yield is 76.65 mg m⁻³ min⁻¹. These results indicate that Mn₂O₃-F is efficient for eliminating toluene even if there is no UV light, exhibiting promising prospects in practical application.

Since H₂O is the source of hydroxyl radicals that is the main oxidants accounting for the photocatalytic degradation of toluene, the influence of relative humidity (RH) on the catalytic performance of Mn₂O₃-F was studied by changing H₂O content in the feed gas. Profiles and histograms in Fig. 5c and d show that the photothermal degradation of toluene and the mineralization efficiency curves rise first and then down with

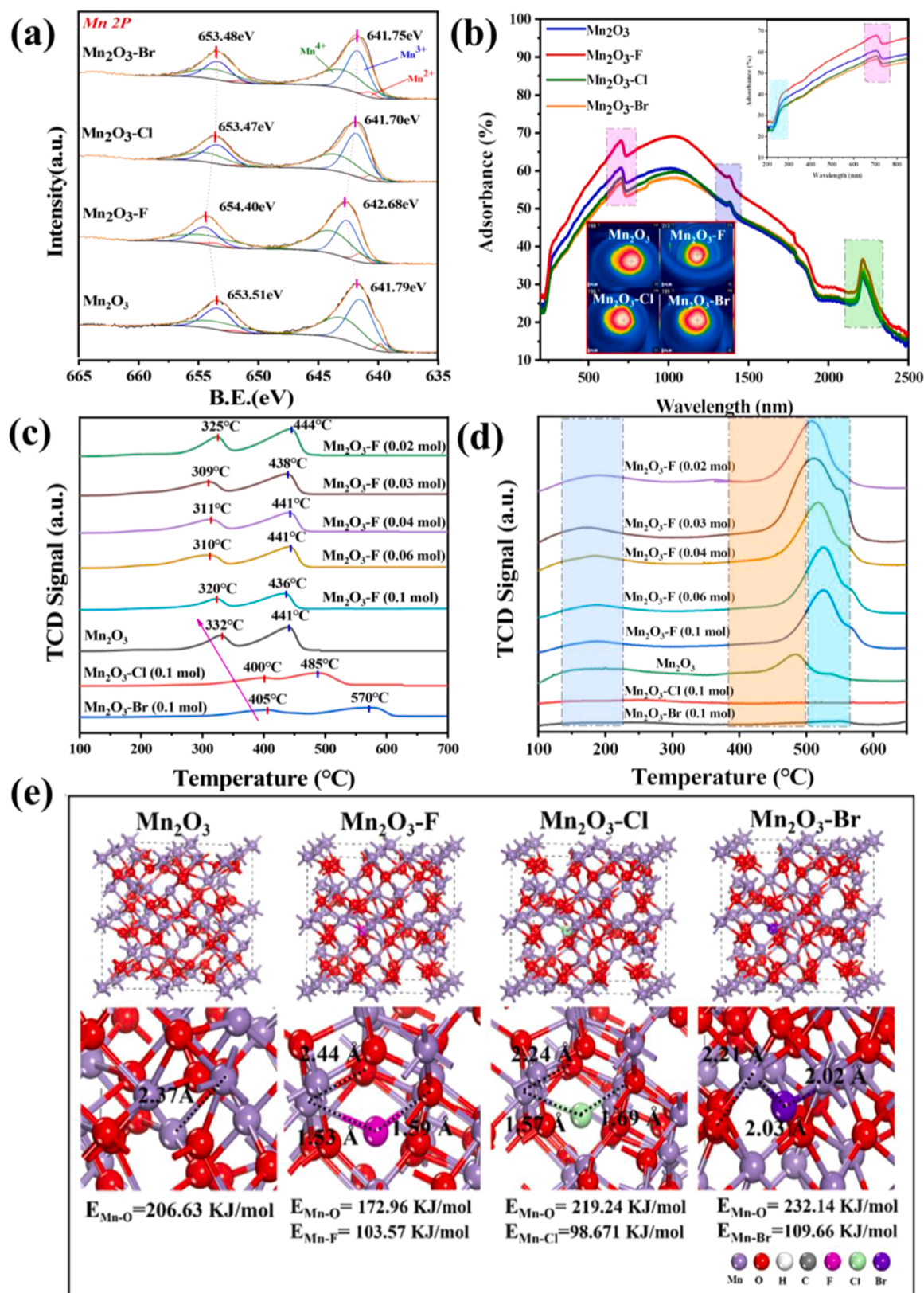


Fig. 3. (a) XPS spectra of Mn 2p, (b) UV-Vis-NIR diffuse reflectance spectra and temperature images of Mn₂O₃, Mn₂O₃-F, Mn₂O₃-Cl, and Mn₂O₃-Br; (c) H₂-TPR, (d) O₂-TPD analysis about Mn₂O₃ and those doped with halogens, (e) calculated band energies of Mn-O, Mn-F, Mn-Cl, and Mn-Br.

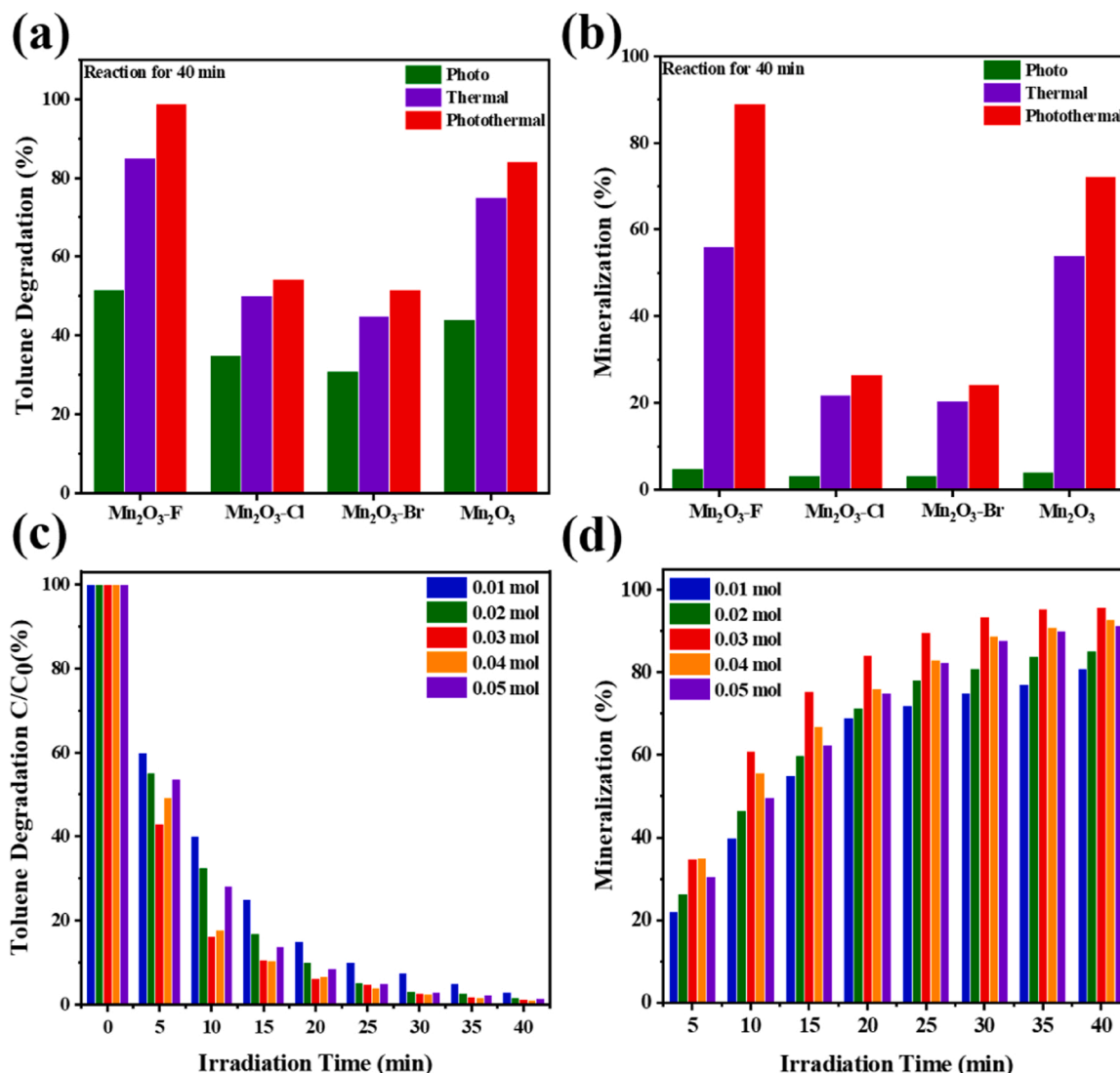


Fig. 4. (a) Degradation percentage of toluene and (b) mineralization degree in 40 min under different conditions including photocatalysis performed at 25 °C (cooled by condensate water), thermal catalysis at 210 °C without lights, and photothermal catalysis under UV–Vis–NIR lights, (c) toluene degradation and (d) mineralization affected by variable F contents. (Air condition: N₂:78%, O₂:21%, and relative humidity: 50%).

increased RH. The degradation efficiency peaks at RH 60%, 98% removal percentage and 94% CO₂ yield are determined. After that, a higher RH leads to delined catalytic activity, for competitive adsorption occurs between excess H₂O and toluene. Moreover, a thin H₂O membrane may cover the active sites on Mn₂O₃ and then scale back the reaction possibility. As the ambient humidity in the air generally ranges from 40% to 80% [55], the outstanding performance in detoxifying toluene makes Mn₂O₃-F propitious in assembling advanced appliances for high-quality indoor air.

Apart from the high activity, a long lifetime is essential for a promising catalyst. Consecutively repeated degradation of toluene using the same catalyst was performed to assess the stability of optimal Mn₂O₃-F. Corresponding results in Fig. S5 depict that Mn₂O₃-F retains its superior activity even in the 10th test, the mineralization is only decreased by 3.2%, confirming its outstanding durability.

The catalytic performance of Mn₂O₃-F (0.03 mol) in degrading toluene with high concentration and variable typical VOCs were studied as well. As shown in Fig. 6 and Table S4, the optimal Mn₂O₃-F (0.03 mol F) exhibits high efficacy in decomposing toluene when its initial concentration ranges from 400 ppm to 1000 ppm. The removal percentage is 98% at 1000 ppm in 40 min, which can reach 100% with prolonged irradiation time. Different gaseous chemicals like

formaldehyde, n-hexane, xylene, and benzene were selected as targets to evaluate the Mn₂O₃-F's practicability under complex conditions. As depicted, formaldehyde, n-hexane, xylene (Initial concentration: 400 ppm) can be completely converted to CO₂ and H₂O. Regarding benzene, the removal percentage is 88% and the mineralization degree is 79.1%, for the symmetric and stable structure of benzene. Although there is a bit of decline, its performance in detoxifying VOCs is still attractive, evidencing its promising prospect in practice. Additionally, comparing Mn₂O₃-F with those reported in literature like Co₃O₄/TiO₂, W doped MnO₂, CeO₂/LaMnO₃, Mn₂O₃/Mn₃O₄/MnO₂ (Table S5), either the removal percentage or mineralization degree of toluene achieved on Mn₂O₃-F is remarkable.

3.4. Oxygen vacancy produced on Mn₂O₃ catalysts

Based on the above catalytic performance of Mn₂O₃ and halogen-Mn₂O₃ catalysts, it is believed that active oxygen species contribute to the accelerated mineralization of toluene. In Fig. 7a, the O 1s XPS spectrum collected from Mn₂O₃ is deconvoluted into three peaks, containing lattice oxygen at 529.5 eV (O_{lattice}), surface adsorption oxygen species (O_{ad}) at 531.0 eV (induced by O_{vacancy}), and adsorbed hydroxyl groups or water at 533.0 eV (O_{OH}) [56]. Among them, O_{ad} species

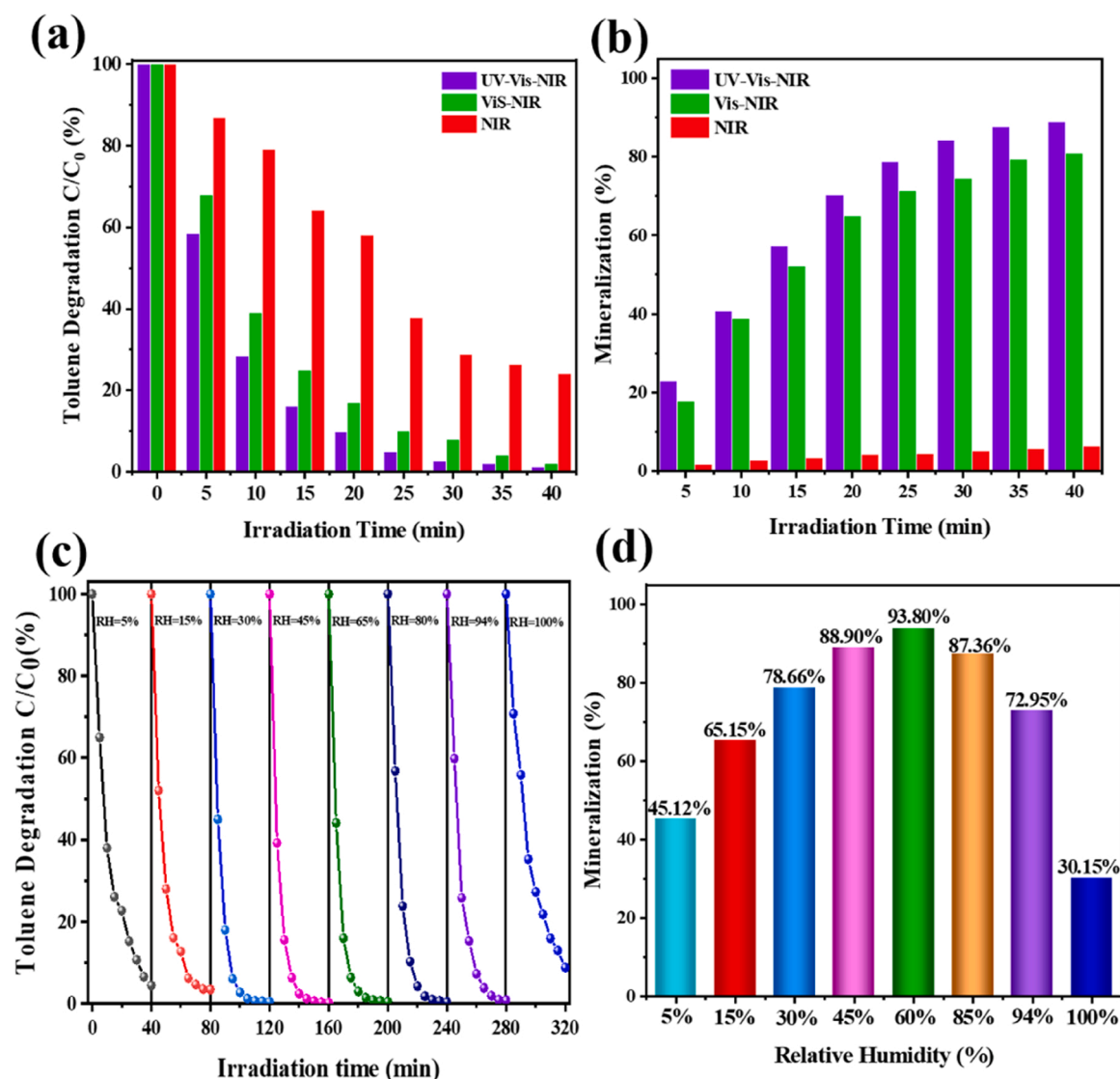


Fig. 5. (a) Toluene removal and (b) mineralization affected by the Mn_2O_3 -F under different wavelength lights, (c) degradation of toluene, and (d) mineralization degree affected by variable relative humidity (RH).

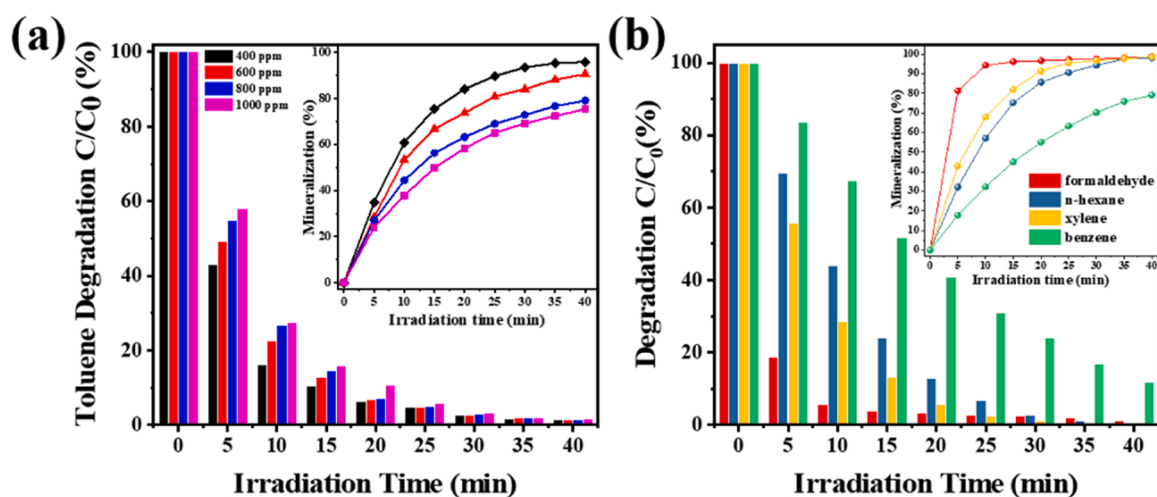


Fig. 6. Toluene removal and mineralization percentage of (a) different concentration toluene and (b) different pollutant species over Mn_2O_3 -F (0.03 mol).

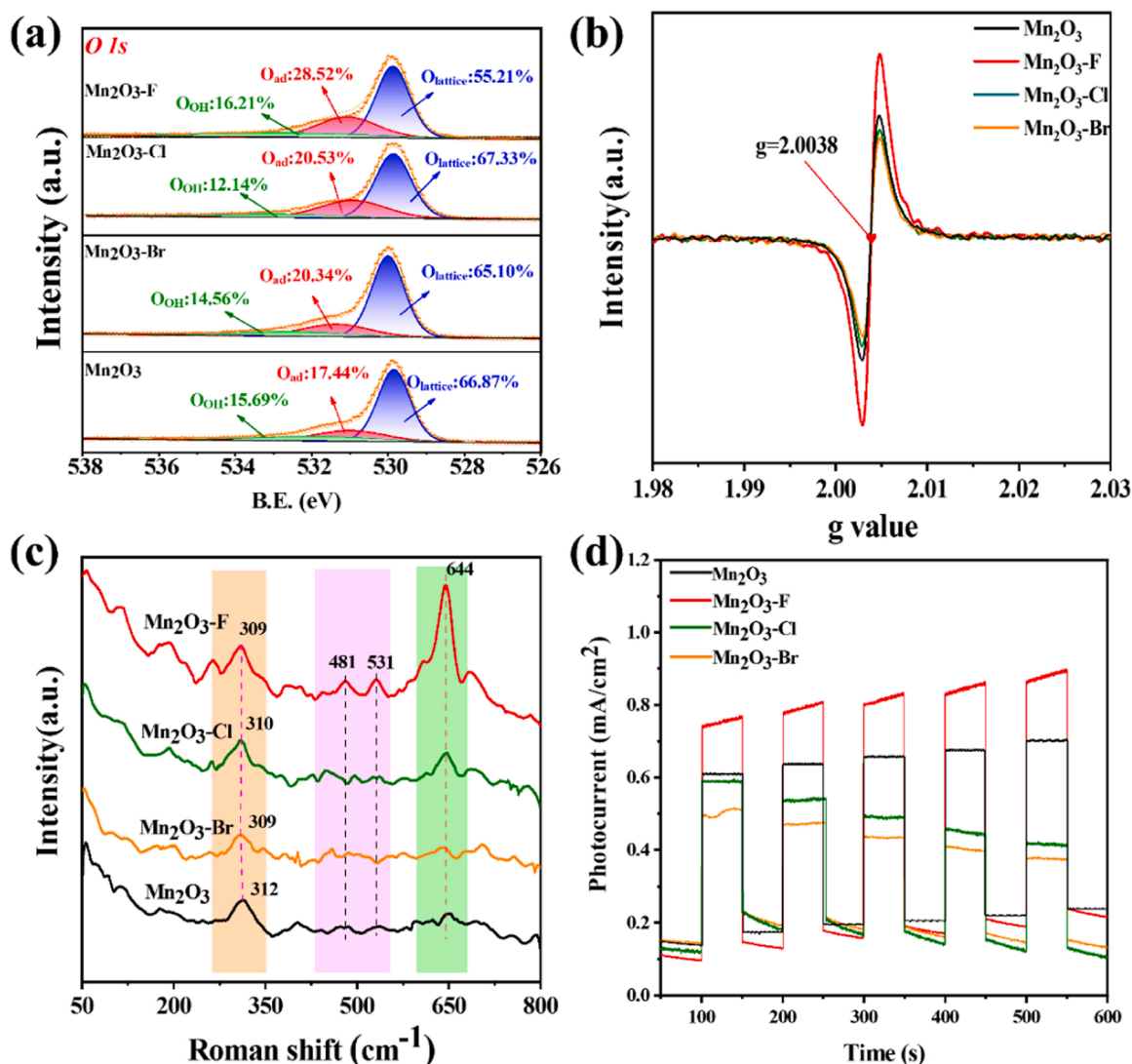


Fig. 7. (a) XPS spectra of O 1s, (b) ESR spectra of oxygen vacancy, (c) Raman spectra, (d) photocurrent intensity.

including O₂⁻, O₂²⁻ and O⁻ are responsible for the catalytic degradation of target molecules [3,27], which depend on the oxygen vacancies (O_{vs}) implanted in the semiconductor. Namely, more oxygen vacancies, more surface adsorbed active oxygen and higher final degradation efficiency. By integrating the peak area in Fig. 7a, the O_{ad} proportion in Mn₂O₃-F is 28.52%, higher than the 17.44% in Mn₂O₃, 20.53% in Mn₂O₃-Cl, and 20.34% in Mn₂O₃-Br, signifying that there are many more O_{vs} in Mn₂O₃-F. Fig. 7b demonstrates the electron spin resonance (ESR) spectra recorded on Mn₂O₃ and Mn₂O₃ catalysts doped with F⁻, Cl⁻, and Br⁻. The most intense ESR signal rendered by Mn₂O₃-F demonstrates that Mn₂O₃ is enriched with O_{vs} due to F⁻ doping. Instead, bringing Cl⁻ and Br⁻ in Mn₂O₃ impedes the O_{vs}'s production because of their passivation effect as mentioned above.

To elaborate the creation of O_{vs} in Mn₂O₃, Raman spectra were collected. As Fig. 7c displays, the peaks observed at 309 cm⁻¹, 481 cm⁻¹, 531 cm⁻¹, and 644 cm⁻¹ are assigned to the asymmetric stretching mode of the bridging oxygen species (Mn-O-Mn). Notably, Mn₂O₃-F exhibits stronger Raman intensity than all the other Mn₂O₃ catalysts, especially the Raman mode centered at 644 cm⁻¹ which is a sign that can prove many more oxygen defects in Mn₂O₃-F [57]. The measurement of transient photocurrent response was carried out to verify the separation of photo-induced carriers in Mn₂O₃ catalysts doped with different halogens (X=F, Cl, Br). As the I-t curves in Fig. 7d depict, Mn₂O₃-F surpasses the pristine ones, Mn₂O₃-Cl, and Mn₂O₃-Br in

generating high-density current.

The relative O_v concentration can be expressed as the average oxidation state (AOS) of Mn 3s in Mn₂O₃ samples, the lower value of AOS, the higher the oxygen vacancy concentration [24], which was calculated based on the multiplet splitting of Mn 3s orbitals according to the following formula:

$$AOS = 8.95 - 1.13\Delta Es(eV)$$

Where ΔEs is the binding energy difference between the main peak and its satellite originated from multiplet splitting in Mn 3s orbitals. The obtained ΔEs of Mn₂O₃, Mn₂O₃-F, Mn₂O₃-Cl, and Mn₂O₃-Br are 5.40, 5.84, 5.59, and 5.47 eV, respectively (Fig. 8). The AOS in Mn₂O₃-F is 2.35 eV, which is the lowest among all the Mn₂O₃ catalysts, revealing its highest O_v content, which is in line with ESR analysis (Fig. 7b).

Furthermore, the O_v formation energies on pristine Mn₂O₃ and halogen-Mn₂O₃ were calculated (Fig. S6). The sequence from high to low is: Mn₂O₃ (1.57 eV) > Mn₂O₃-Br (1.06 eV) > Mn₂O₃-Cl (0.696 eV) > Mn₂O₃-F (0.272 eV). It's known that doping with heteroatoms in crystals can prompt lattice distortion, damage its perfect and stable construction and create defects there. Therefore, all the halogen-Mn₂O₃ catalysts show lower O_v formation energy than the pristine Mn₂O₃. The lowest O_v formation energy in Mn₂O₃-F indicates that O atoms are the most vulnerable to escaping from the stretched Mn-O bonds. As for

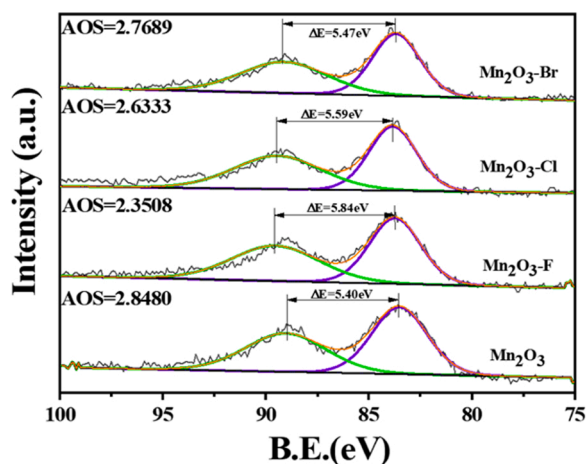


Fig. 8. High resolution on XPS spectra of Mn 3s in Mn_2O_3 and halogen doped Mn_2O_3 .

$\text{Mn}_2\text{O}_3\text{-Cl}$ and $\text{Mn}_2\text{O}_3\text{-Br}$, although the O_v formation energy is decreased, the big-size Cl^- and Br^- can block those O_v s, presented as deteriorated catalytic activity despite the deformed crystal lattice and decreased O_v formation energy.

The charge density difference (CDD) and electron localization function (ELF) maps around the halogen (X: F, Cl, Br) atoms are analyzed to further investigate the localization behavior of electrons when oxygen vacancies are formed as the images show, when F atoms substitute O sites, many electrons localize around the F atoms and fewer

electrons are concentrated on coordinated O atoms. On the contrary, O sites substituted by Cl and Br atoms concentrate fewer electrons than those adjacent O atoms, which indicates the adjacent Mn-O bonds concatenate too hard to be broken up. Comparing the ELF maps, the electron localization area around the F atom enlarges as an adjacent oxygen vacancy appears, displayed as the circled area in Fig. 9. Oxygen vacancies can serve as the major exchange and transfer centers for electrons, in which the yellow and blue isosurfaces mean charge accumulation and depletion in the space.

3.5. Probable mechanism involved in photothermal degradation of toluene

Generally, reactive oxygen species like $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ are responsible for the decomposition of toluene in both photocatalysis and photothermal catalysis [58]. The EPR signals of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ recorded on different Mn_2O_3 are displayed in Fig. 10a and b, which are silent in darkness, and sensitive under irradiation. Comparatively, these specific peaks on $\text{Mn}_2\text{O}_3\text{-F}$ are much intenser than other catalysts, relational contents of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ on $\text{Mn}_2\text{O}_3\text{-F}$ reaches 2.29×10^{-5} and 3.77×10^{-6} mol/L, respectively (Table S6). the amount of $\bullet\text{O}_2^-$ is almost 10 times that $\bullet\text{OH}$, which validates that the abundant O_v s in $\text{Mn}_2\text{O}_3\text{-F}$ contribute to adsorb many more O_2 from the air, delivering stronger signals with prevailing other Mn_2O_3 catalysts.

The superior catalytic activity on $\text{Mn}_2\text{O}_3\text{-F}$ can be illustrated by the adsorption behaviors of O_2 , H_2O , and toluene molecules through DFT calculations. The adsorption energies of O_2 and H_2O molecules on $\text{Mn}_2\text{O}_3\text{-F}$ are the lowest, -2.655 eV and -2.069 eV, respectively, which indicates O_2 and H_2O can be tightly adsorbed on $\text{Mn}_2\text{O}_3\text{-F}$ surface and activated there to form $\bullet\text{O}_2^-$ and $\bullet\text{OH}$. Since all the adsorption is

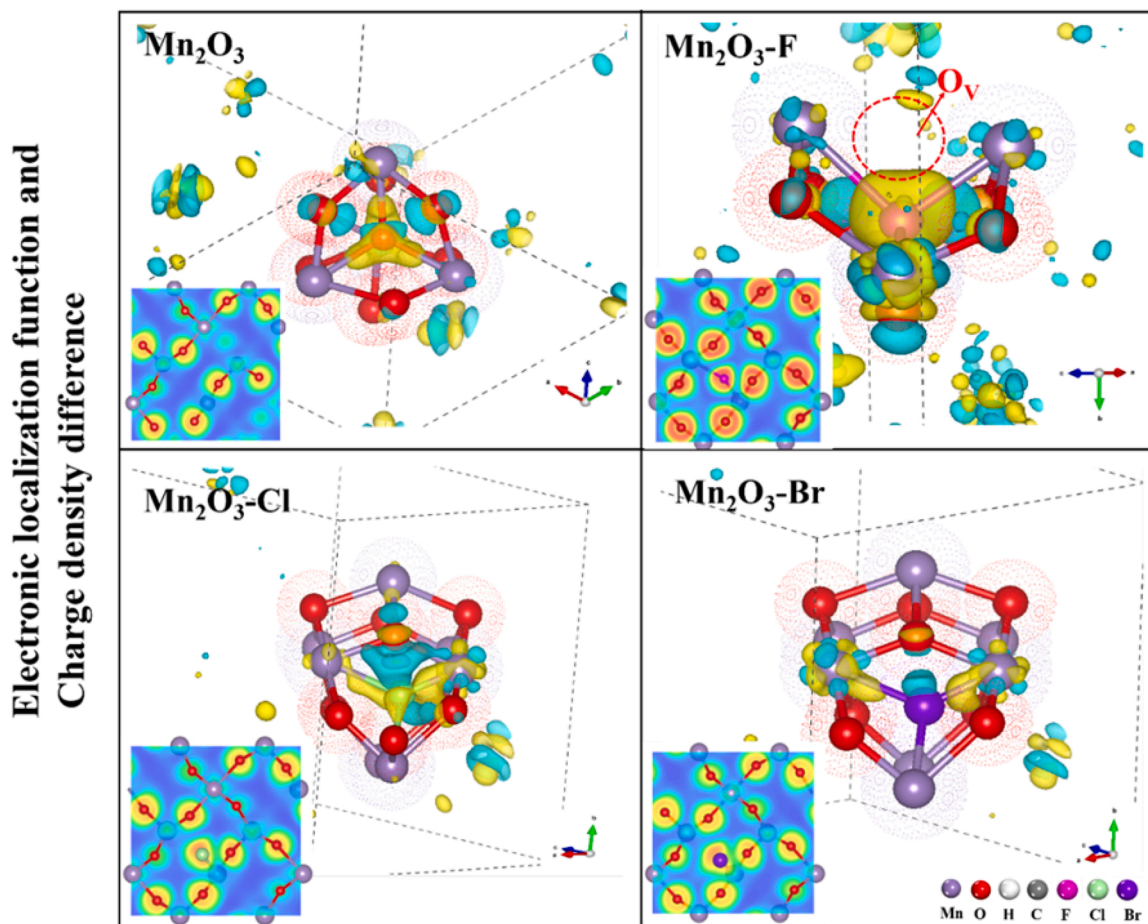


Fig. 9. Electronic localization function and charge density difference on Mn_2O_3 and halogen- Mn_2O_3 catalysts.

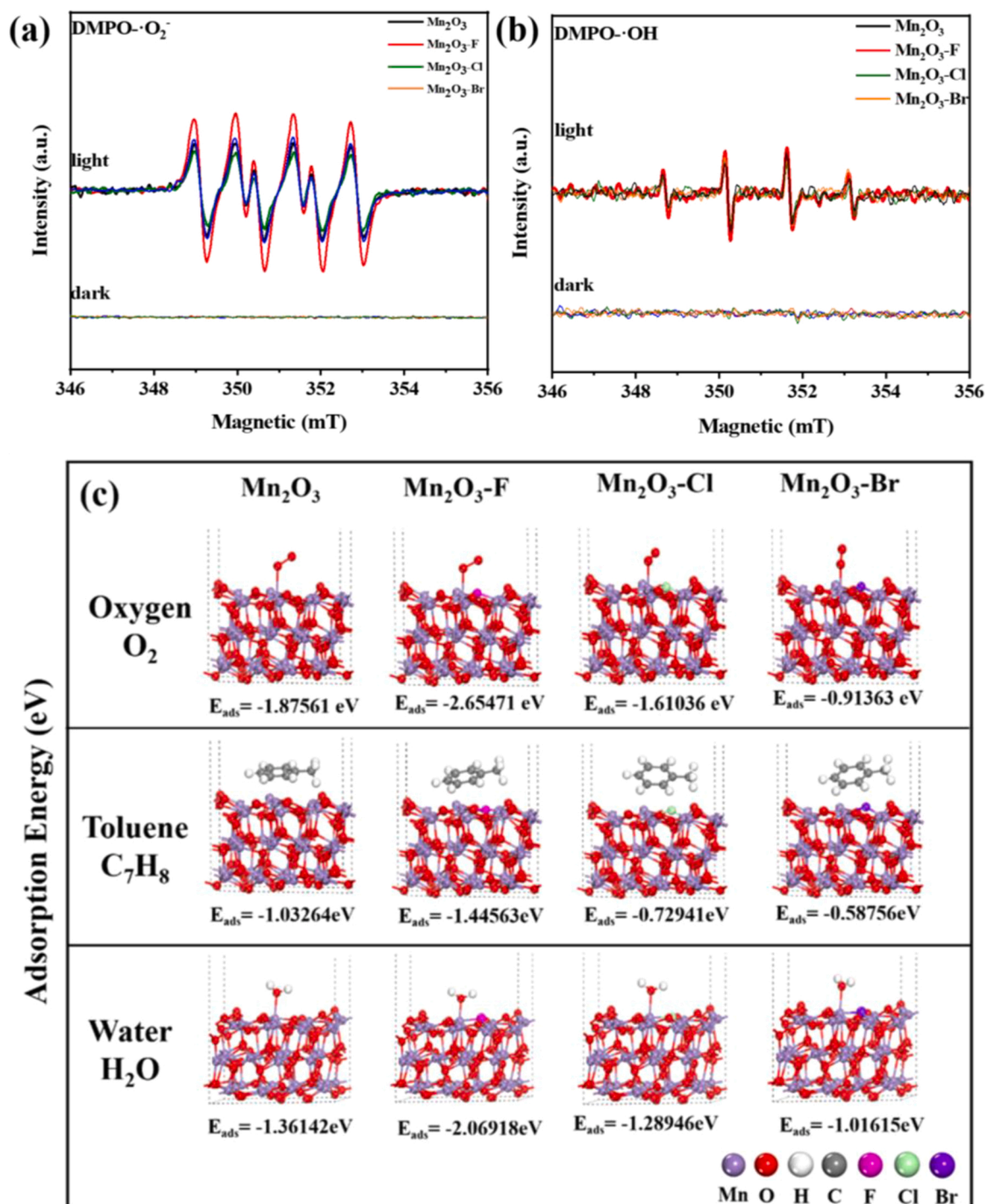


Fig. 10. DMPO spin-trapping EPR spectra of (a) $\text{DMPO} \cdot \text{O}_2^-$ and (b) $\text{DMPO} \cdot \text{OH}$; (c) theoretical calculations (DFT) for adsorption energy of O_2 , toluene, H_2O over different Mn_2O_3 .

exothermic, a lower toluene adsorption energy means a higher affinity between toluene gases and catalyst, suggesting that toluene will be more easily oxidized by the reactive oxygen species on the catalyst interface [59]. As Fig. 10c shows, the E_{ads} (-1.446 eV) of toluene on $\text{Mn}_2\text{O}_3\text{-F}$ is the lowest one, for the oxygen vacancies endows specific area with thick electron clouds that facilitate the adsorption of toluene. The above discoveries manifest that O_2 , H_2O , and toluene molecules on the $\text{Mn}_2\text{O}_3\text{-F}$ interface are easier to be anchored. As a result, the reaction probability between reactive oxygen species and toluene is greatly promoted.

To clarify the process of toluene degradation over $\text{Mn}_2\text{O}_3\text{-F}$, toluene

molecules and the intermediates on the catalyst surface were identified. Fig. S7 shows that the specific peak assigned to toluene is extremely high at the beginning, which disappears when the catalysis is finished at 40 min. There are some products from toluene degradation, containing benzaldehyde ($m/z = 106$), benzyl alcohol ($m/z = 108$), benzoic acid ($m/z = 122$), 1,3,5-trihydroxy benzene ($m/z = 126$), p-Hydroxybenzoic acid ($m/z = 138$), 2, 4-dihydroxycaproic acid ($m/z = 148$).

MS spectra of intermediates collected during the catalysis process at different times are shown in Fig. S8. 10 min after the beginning, many organic products appear, among which the highest signal values are indexed to benzaldehyde ($m/z = 106$) and benzyl alcohol ($m/z = 108$),

and the signal value of toluene ($m/z = 92$) is remarkably decreased.

20 min later, hydroquinone ($m/z = 110$), 1,3,5-trihydroxy benzene ($m/z = 126$), p-Hydroxybenzoic acid ($m/z = 138$), and 2,4-dihydroxycaproic acid ($m/z = 148$) are produced gradually while the amounts of benzaldehyde and benzyl alcohol ($m/z = 108$) minimize. When the reaction is completed, 1,3,5-trihydroxy benzene ($m/z = 126$), and 2, 4-dihydroxycaproic acid ($m/z = 148$) appear as main products.

Based on the aforementioned results, probable degradation pathways were proposed. As Fig. 11a shows, the methyl carbon as the electron-donating group is attacked by $\bullet\text{OH}$, and one of the hydrogen atoms in methyl falls off to form benzyl alcohol. Resultantly, the equilibrium state of the electrons inside the benzene ring is disturbed, and the stable carbon ring is activated with thickened electron density. Benzyl alcohol can be further oxidized to benzaldehyde by $\bullet\text{O}_2^-$ and O^- , and then to benzoic acid. The structural stability of the benzene ring is further damaged with the further loss of electrons along with the carbon group outside the benzene ring. As the carboxyl is an electron-denoting group, the benzene ring is further triggered with thickened electron clouds, and thus ready to accept the attacks from h^+ , $\bullet\text{O}_2^-$ and O^- . Afterward, the activated benzene ring and carboxyl are attacked by $\bullet\text{O}_2^-$

and O^- to form 1,3,5-trihydroxy benzene or hydroquinone, which transforms into CO_2 and H_2O ultimately.

The mechanism involved in the photothermal degradation of toluene is schematically depicted in Fig. 11b. As shown, under irradiation, the temperature of $\text{Mn}_2\text{O}_3\text{-F}$ can be approached to 213°C , providing energy for the thermal motion in those reactions happening on $\text{Mn}_2\text{O}_3\text{-F}$. Oxygen vacancies induced by halogen doping are demonstrated in the peach rectangle. F atoms that replace O atoms attract the shared electrons from Mn to itself. Therefore, the deviated charge center stretches the adjacent Mn-O bonds and boosts the generation of abundant oxygen vacancies, helping to activate the adsorbed O_2 to $\bullet\text{O}_2^-$. Besides that, the redox couples of $\text{Mn}^{2+}/\text{Mn}^{3+}$, $\text{Mn}^{3+}/\text{Mn}^{4+}$ contribute to producing $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ (green rectangle) for decomposing target toluene molecules. The above findings indicate that employing photothermal catalysts is a sustainable and efficient strategy to remove VOCs from the air.

4. Conclusion

The impact of representative halogen elements (F, Cl, Br) on regulating the activity of Mn_2O_3 catalysts was investigated through

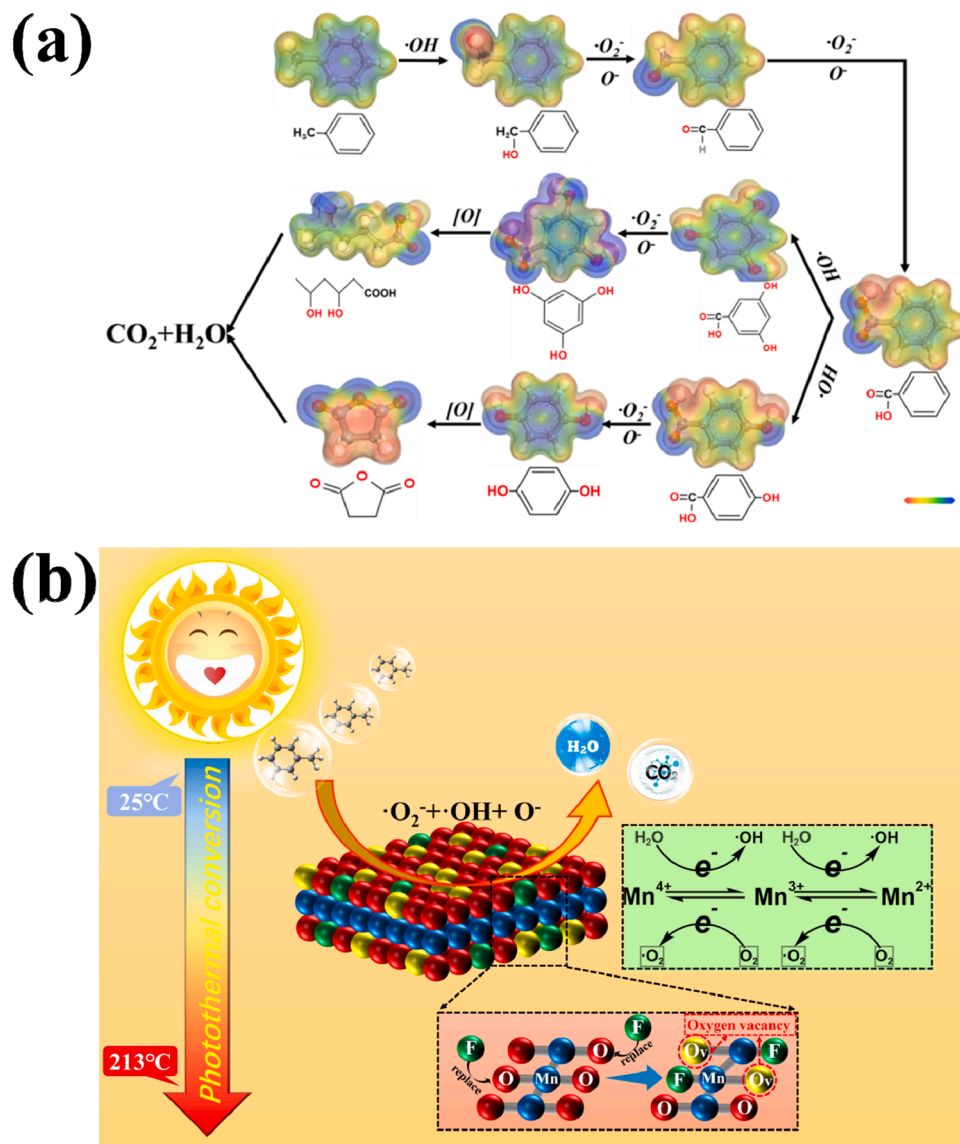


Fig. 11. (a) Proposed pathway of the photothermal catalytic degradation of toluene over $\text{Mn}_2\text{O}_3\text{-F}$. Electron density along carbon skeletons are visualized with red representing high electron-density area and blue representing the low electron-density area, (b) Schematic photocatalytic mechanism of toluene degradation with $\text{Mn}_2\text{O}_3\text{-F}$ catalyst.

photothermal degradation of toluene. Among F⁻, Cl⁻ and Br⁻, F⁻ has a similar diameter with O²⁻, and the highest electronegativity. It's easy and available for F⁻ to replace O²⁻ in Mn₂O₃ lattices. Owing to the marvelous ability to draw electrons, F⁻ dopant gives rise to the derivation of electron center between F-Mn bonds, which is far away from Mn ions, and therefore leads to the stretching of adjacent Mn-O bonds. As stretched Mn-O bonds weaken the binding force toward O atoms, which are prone to escape. Resultantly, the numbers of active Mn²⁺ and Mn⁴⁺ are increased and the distorted crystal lattices provide abundant oxygen vacancies. As for Cl⁻ and Br⁻, the big size makes them difficult to supplant the O atoms in Mn₂O₃ lattice, and the active sites can be covered when they are adsorbed on the Mn₂O₃ surface, exhibiting a deactivated effect on Mn₂O₃ activity in the photothermal degradation of toluene. Some Cl⁻ and Br⁻ can be doped in Mn₂O₃, but their lower electronegativity and big dimension lead to the shortened Mn-O bonds, posing a contrary influence on engineering Mn₂O₃ in comparison with F⁻. This work figures out the detailed reason for the influence of halogens on Mn₂O₃ catalysts in-depth and will enrich the scientific foundation of photothermal catalysts for VOC removal.

CRediT authorship contribution statement

Xiao Yu: Methodology, Investigation, Writing – original draft. **Mengyi Shi:** Investigation. **Yixuan Fan:** Conceptualization. **Wei Liu:** Investigation. **Lixia Yang:** Supervision, Writing – review & editing. **Jie Zhang:** Theoretical calculation. **Weili Dai:** Project administration. **Shuqu Zhang:** Methodology. **Xubiao Luo:** Resources. **Lei Zhou:** Methodology. **Shenglian Luo:** Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2022.121236](https://doi.org/10.1016/j.apcatb.2022.121236).

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